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SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEX SYSTEMS WITH NOVEL SOLID STATE PROPERTIES

L.V. Interrante
Principal Investigator

FINAL SCIENTIFIC REPORT
Period Covered: 1 April 1979 - 30 March 1982

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AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Directorate of Chemical Sciences
Bolling Air Force Base, Bldg. 410
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FOREWORD

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These various compounds have been studied using electrical conductivity, magnetic susceptibility, and other solid state property measurement techniques. In addition, their crystal structures have been characterized using single crystal x-ray diffraction methods. The results provide new information regarding the solid state interactions in metal complex-containing systems and suggest the promise of such systems as a source of solid state materials with novel magnetic and electronic properties.

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Section 1

INTRODUCTION

The primary objectives of this research program were: (1) to elucidate synthetically useful structure-property relationships that ultimately will enable the directed synthesis of transition metal complex systems with desired solid state properties, and (2) to synthesize and characterize new materials with novel solid state electrical and/or magnetic properties.

In pursuit of these objectives we selected for study particular types of transition metal complexes which have structures and properties appropriate for extended solid state intermolecular interactions and which can be structurally modified so as to permit a systematic investigation of molecular structure-solid state property relationships. The systems chosen include the bis-dithiolene metal complexes, which we have used previously as π -acceptors in the preparation of π -donor-acceptor (π -D·A) compounds with novel magnetic and electrical properties⁽¹⁾ and various macrocyclic metal complexes which were considered to be promising candidates for use as π -donors in π -D·A compound formation.

The work on the bis-dithiolene metal complexes has focused, in particular, on the further characterization and elaboration of the $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ series of compounds which were found in our earlier studies to exhibit novel magnetic properties. Included among these compounds are the first examples of one-dimensional magnetic systems which undergo the spin-Peierls transition, a new magnetoelastic effect first discovered in our laboratory in 1975 and currently the object of considerable scientific attention worldwide⁽²⁾. The studies of the macrocyclic metal complex systems involved the use of both nitrogen and sulfur containing ligands and included efforts to synthesize new macrocyclic systems as well as the preparation, structural characterization, and physical property study of selected π -D·A compounds. In addition, a novel iridium(I)

complex was prepared using a new organic ligand system and examined as a source of conductive 1-D materials, employing iodine to partially oxidize the complex units.

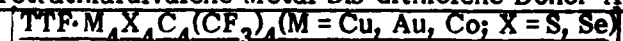
Our approach to the investigation of these systems has involved both the synthesis and characterization of new compounds and the detailed structural and physical study of selected systems in collaboration with scientists at other institutions as well as in our own laboratories. In those cases where evidence for novel solid state properties has been obtained, as for example with the $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ compounds, a full range of molecular structural variations has been explored, both in order to generate further examples of novel materials and as a means of obtaining information regarding the systems and phenomena in question. The results of these studies are summarized in the following section.

Section 2

SUMMARY OF PROGRESS

I. π -Donor Acceptor (π -D·A) Compounds Derived from Planar Metal Complexes

A. Tetrathiafulvalene Metal Bis-dithiolene Donor-Acceptor Compounds



These compounds were first prepared in our laboratory in 1975 under a previous AFOSR contract as part of a general exploratory survey of π -donor-acceptor (π -D·A) compounds derived from the interaction of the organic π -donor, tetrathiafulvalene (TTF), with various bis-dithiolene metal complexes.⁽¹⁾ The products of this interaction, in the case of the $\text{MS}_4\text{C}_4(\text{CF}_3)_4$ complexes, are fully charge-transferred 1:1 π -D·A compounds of the type, $\text{TTF}^+\text{MS}_4\text{C}_4(\text{CF}_3)_4^-$, which typically exhibit low electrical conductivity but whose magnetic properties indicate the existence of 1-D cooperative magnetic interactions in the solid state.

The $\text{M} = \text{Cu}$ and Au derivatives of this type have proven to be of particular interest with respect to their magnetic properties and are currently the object of much attention in scientific laboratories both in Europe and in the U.S. as members of a very limited group of compounds which have been found to exhibit the "spin-Peierls transition". This transition was anticipated theoretically almost two decades ago, but only first realized experimentally in 1975 as a consequence of the synthesis and study of the $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ ($\text{M} = \text{Cu, Au}$) compounds.⁽²⁾ It is basically a new magnetoelastic effect in which a parallel array of 1-D antiferromagnetic chains couples with a 3-D lattice to drive a 3-D lattice distortion which results in a dimerization of the chains and a coupling of the spins to produce a singlet ground state.

In the case of the $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ ($\text{M} = \text{Cu, Au}$) compounds, a wide variety of physical measurements, including x-ray and neutron diffraction, have been used over the past several years to study this transition and the dimerized phase which

results from it. The information that these measurements have provided have helped to verify and further develop theoretical understanding in this area which has led in turn to interesting predictions regarding new phenomena and phases in these systems. In particular, in 1978 the prospect of an unusual field dependence for this transition was realized and the subsequent investigation of the $\text{TTF} \cdot \text{CuS}_4\text{C}_4(\text{CF}_3)_4$ system under high magnetic fields gave evidence for a new phase or (phases) at low temperatures.⁽³⁾ These new phases appear to be a direct consequence of changing k_F (the pseudofermion Fermi wave vector) for the spin-Peierls system by the magnetic field. The new phases may be either higher order commensurate phases or an incommensurate phase, but their detailed nature remains uncertain. Further experimental and theoretical work in this area is needed, and in particular direct structural study of the new phases by neutron or x-ray diffraction would be highly desirable.

Theoretical studies have indicated that the magnetic field above which the non-magnetic spin-Peierls phase is completely repressed and the new phase(s) appear, scales with the zero-field transition temperature.⁽³⁾ Therefore, the $\text{TTF} \cdot \text{CuS}_4\text{C}_4(\text{CF}_3)_4$ system, for which the transition temperature is 12°K , requires the highest magnetic fields ($\geq 125\text{KG}$) for the observation of these new phases. For the related $\text{TTF} \cdot \text{AuS}_4\text{C}_4(\text{CF}_3)_4$ and $\text{TTF} \cdot \text{CuSe}_4\text{C}_4(\text{CF}_3)_4$ compounds, which exhibit spin-Peierls transitions in zero field at 2°K and 6°K respectively, these phases should be observable at considerably lower magnetic field strengths, permitting their more convenient and detailed study using structural and physical property measurement methods. Therefore, our more recent efforts in this area have focused on the further synthesis, single crystal preparation and study of these two members of the spin-Peierls family of compounds.

In 1981 a sample of the perdeutero- $\text{TTF} \cdot \text{AuS}_4\text{C}_4(\text{CF}_3)_4$ compound was sent to the Kammerling Onnes Laboratory in the Netherlands for studies of the

specific heat and high field susceptibility in the regime of low temperature and high magnetic field in which the new phases were expected to appear. The results of these studies have recently been published in the form of a full paper in the journal Physical Review.⁽⁴⁾ A key result is the observation of a striking similarity in the phase behavior of the $\text{TTF} \cdot \text{AuSe}_4\text{C}_4(\text{CF}_3)_4$ compound and two other previously well-studied examples of "spin-Peierls compounds", $\text{TTF} \cdot \text{CuSe}_4\text{C}_4(\text{CF}_3)_4$ and the purely organic system $(\text{MEM})(\text{TCNQ})_2$ (MEM = methylethylmorpholinium). These "universal" aspects obtain, despite considerable differences in lattice structure and a variation in the zero-field, spin-Peierls transition temperature of a factor of 10.

The $\text{TTF} \cdot \text{CuSe}_4\text{C}_4(\text{CF}_3)_4$ derivative was originally prepared in small quantities, using a sample of $\text{Et}_4\text{N}^+\text{CuSe}_4\text{C}_4(\text{CF}_3)_4^-$ obtained from Professor B. Hoffman of Northwestern University. During the current contract period we have obtained our own source of the $(\text{CF}_3)_2\text{C}_2\text{Se}_2$ ligand, by means of a high-temperature reaction between hexafluorobutyne and Se vapor, and have used it to prepare a larger quantity of the $\text{CuSe}_4\text{C}_4(\text{CF}_3)_4^-$ complex and its TTF^+ salt. By slow cooling of acetonitrile solutions of this material, we have now obtained large single crystals suitable for detailed structural studies. Such studies will be carried out this summer by Dr. David Moncton of the Brookhaven National Laboratory using both x-ray and neutron diffraction methods in a continuing effort to learn more about the unusual phase behavior of this class of materials and, in particular, to obtain the first direct structural characterization of the high field spin-Peierls phase(s).

In the course of this preparation of the $\text{TTF} \cdot \text{CuSe}_4\text{C}_4(\text{CF}_3)_4$ compound we have also isolated a new compound for which elemental analyses indicate a $\text{TTF}_{1.125}\text{CuSe}_4\text{C}_4(\text{CF}_3)_4$ empirical formula. Preliminary single crystal x-ray precession measurements, as well as magnetic susceptibility and d.c. conductivity

studies were carried out on this compound, indicating distinct differences in crystal structure and physical properties between this and the $\text{TTF} \cdot \text{CuSe}_4\text{C}_4(\text{CF}_3)_4$ derivative. This new compound does not exhibit a spin-Peierls transition but instead is diamagnetic from room temperature down to 4K. A large single crystal was mounted for 4-probe d.c. conductivity measurements; however, it was found to be too poorly conducting to allow a determination of the conductivity by this method (presumably $< 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$). The preliminary results obtained thus far suggest an unusual molecular association of the TTF^+ units in this structure, such that the ground state of the system is non-magnetic.

In an effort to extend the $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ series of compounds to include the corresponding Co derivative, the compound $\text{Et}_4\text{N}^+ \text{CoS}_4\text{C}_4(\text{CF}_3)_4^-$, containing the non-magnetic $\text{CoS}_4\text{C}_4(\text{CF}_3)_4^-$ ion, was prepared and combined with $\text{TTF}^+ \text{Cl}^-$ in the same manner which was used to obtain the other $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ compounds. Elemental analysis of the product of this reaction corresponds most closely to a $\text{TTF} \cdot \text{CoS}_4\text{C}_4(\text{CF}_3)_4$ formula; however, x-ray powder diffraction results indicate that the crystal structure of this compound is unlike that of any of the earlier compounds of this type. The magnetic susceptibility of this material is also unusual for a $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ compound, suggesting a singlet ground state with a thermally accessible triplet state at room temperature. A model of exchange coupled TTF^+ dimers may be appropriate for this system; however, any definite conclusions regarding the structure and the magnetic coupling mechanism must await a crystal structure study. Such an investigation is planned for both this system and the new $\text{TTF}_{1.125} \cdot \text{CuSe}_4\text{C}_4(\text{CF}_3)_4$ phase in the coming months.

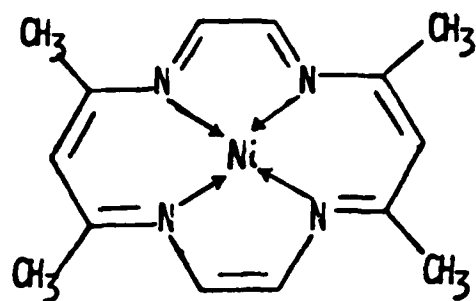
A further justification for a detailed structural study of the $\text{TTF} \cdot \text{CoS}_4\text{C}_4(\text{CF}_3)_4$ compound comes from preliminary measurements of its electrical conductivity using polycrystalline samples. The value obtained for the electrical

conductivity at room temperature, $8 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, is unusually high for the $\text{TTF} \cdot \text{MS}_4\text{C}_4(\text{CF}_3)_4$ family of compounds, which are, in general, good electrical insulators. The model of an extended chain of TTF^+ units, perhaps comprised of loosely associated TTF^+ dimers, is among the several interesting structural possibilities which are suggested by these results.

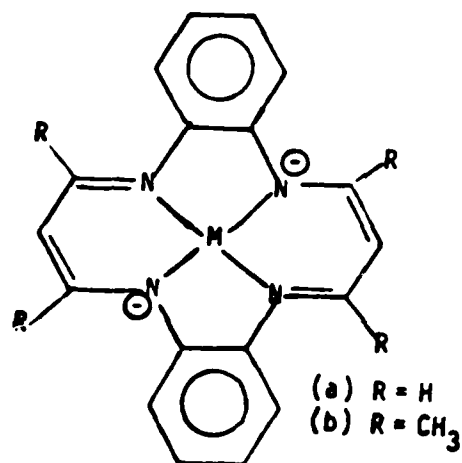
II. Synthesis of New Transition Metal Complex Systems

A. π -Donor-Acceptor Compounds Derived from Macrocyclic Metal Complexes

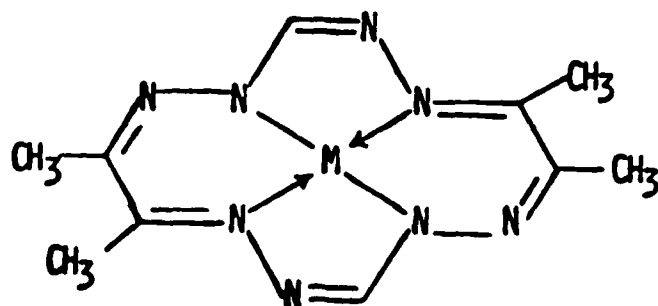
Our efforts to develop new molecular solids with novel electrical and magnetic properties has centered during the past three years on the synthesis of certain macrocyclic metal complexes for use, mainly as π -donors, in the formation of π -donor-acceptor (π -D·A) compounds. The tetraazamacrocyclic nickel compound illustrated in Figure 1a, nickel 1,4,8,11-tetraza-5,7,12,14-tetramethyl(14)-annulene $[\text{Ni}(\text{TATMA})]^{(5)}$ was prepared by Dr. Patrick Cassoux of the CNRS Laboratory in Toulouse, France during a five-month stay in our laboratory during 1979 as a G.E. Research Fellow. This compound was used as a π -donor to synthesize new π -D·A derivatives with both nickel bis-(ethylene-1,2-dithiolene) ($\text{NiS}_4\text{C}_4\text{H}_4$) and the organic π -acceptor, tetracyanoquinodimethane (TCNQ). On the basis of elemental analyses, a $[\text{Ni}(\text{TATMA})]_2\text{A}$ (where $\text{A} = \text{TCNQ}$ or $\text{NiS}_4\text{C}_4\text{H}_4$) molecular formula has been assigned to these compounds. Both compounds are semiconductors ($\sigma_{25} = 10^{-3}$ and $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$, respectively) and exhibit magnetic properties which indicate intermolecular association in the solid state. In particular the $\text{NiS}_4\text{C}_4\text{H}_4$ derivative is paramagnetic with a Curie law constant appropriate for one electron per formula unit whereas the TCNQ compound is diamagnetic. Since the $\text{Ni}(\text{TATMA})^+$ and A^- species which, on the basis of redox potentials, are expected to be present in these compounds should each carry a single unpaired electron, these results indicate the presence of magnetically coupled dimers or extended magnetic interactions in the $[\text{Ni}(\text{TATMA})]_2\text{A}$ compounds.



Ia.



Ib.



Ic.

FIGURE 1. Macrocyclic tetra- and octa-aza [14] annulene metal complexes

Recent work on these compounds have included efforts to determine their crystal structures by using x-ray diffraction methods. Dr. John Kasper in our laboratory has carried out preliminary single crystal x-ray diffraction measurements on both compounds and a full 3-D structural determination of the $[\text{Ni}(\text{TATMA})]_2\text{NiS}_4\text{C}_4\text{H}_4$ derivative is now near completion at the CNRS Laboratory in Toulouse. This compound is of particular interest as the first π -D-A compound which contains metal complexes as both the π -donor and π -acceptor. It crystallizes in the space group $C2/m$ with $a = 26.50 \text{ \AA}$, $b = 14.12 \text{ \AA}$, $c = 10.199 \text{ \AA}$, and $\beta = 115.35^\circ$. The structural arrangement of the D and A units is quite similar to that which was found earlier for the compound $\text{TTF}_2\text{NiS}_4\text{C}_4\text{H}_4$ ⁽¹⁾ with 1-D chains of stacked $\text{Ni}(\text{TATMA})$ units comprised of eclipsed $[\text{Ni}(\text{TATMA})^+]_2$ dimers separated by uncharged $\text{Ni}(\text{TATMA})$ molecules and a 2-D sheet of unstacked $\text{NiS}_4\text{C}_4\text{H}_4^-$ species. The presence of these essentially non-interacting, paramagnetic $\text{NiS}_4\text{C}_4\text{H}_4^-$ species has been evidenced by both the magnetic susceptibility measurement and an esr study on a single crystal of the $[\text{Ni}(\text{TATMA})]_2\text{NiS}_4\text{C}_4\text{H}_4$ compound by Dr. Cassoux. The remaining neutral $\text{Ni}(\text{TATMA})$ unit is found alongside the $[\text{Ni}(\text{TATMA})]^{0,1+}$ chains with its molecular plane oriented perpendicular to both the other $[\text{Ni}(\text{TATMA})]^{0,1+}$ and the $\text{NiS}_4\text{C}_4\text{H}_4^-$ units.

As concluded in the case of the $(\text{TTF})_2\text{NiS}_4\text{C}_4\text{H}_4$ system,⁽⁶⁾ the thermally activated conductivity observed for the $[\text{Ni}(\text{TATMA})]_2\text{NiS}_4\text{C}_4\text{H}_4$ compound probably arises from excitation of electrons from the bound electron pair associated with the $[\text{Ni}(\text{TATMA})^+]_2$ intermolecular "bond" into conduction band states associated with the 1-D stacks of the $[\text{Ni}(\text{TATMA})]^{0,1+}$ units. A suitable crystal for structural studies has recently been obtained for the $\text{Ni}(\text{TATMA})_2 \text{TCNQ}$ system and a complete 3-D x-ray diffraction study of this material is also planned for the near future.

Efforts to extend this series of compounds to include other complexes of the TATMA ligand have also been undertaken as part of a continuing collaborative interaction with Dr. Cassoux. Dr. Cassoux has recently prepared the corresponding Cu(TATMA) complex as well as the dibenzotetraaza- and octaazaannulene nickel(II) complexes I B(a) and I C and has investigated their reactions with both TCNQ and $\text{NiS}_4\text{C}_4\text{H}_4$. Unfortunately, in these cases either no reaction occurred or only decomposition products were obtained on mixing the various donors and acceptors and we were not able to isolate stable π -D·A compounds. This work is still in progress with principal focus on the preparation of the Pd and Pt(TATMA) complexes and their use in π -D·A compound formation. This collaborative effort with Dr. Cassoux has been aided recently by the award of a NATO Grant for international collaboration in research. The award will provide support for travel between the principal investigators' laboratories during the latter half of 1982.

Finally, two potential synthesis routes to the sulfur macrocycle II illustrated in Figure 2 using transition metal ions as a "template" have been explored. This compound was sought as a possible precursor to a new type of planar highly conjugated sulfur-containing macrocyclic systems (structures III, IV) which we intended to use in the preparation of conductive molecular solids. The first reaction attempted involved the prior preparation of a new tetrathiolato-platinum complex (structure I, $\text{M} = \text{Pt}$) which was to serve as the reaction template for the construction of the sulfur macrocycle. The addition of the disodium salt of o-xylyl- α, α' -dithiol to the PtCl_4^{2-} complex in ethanol yielded a highly moisture and air sensitive material which decomposed to give metallic Pt on attempting to purify and characterize it. An alternative procedure was then tried using a known cobalt(II) complex of the o-xylyl- α, α' -dithiolato ligand (I, $\text{M} = \text{Co}$) as the starting material for the template reaction. Inspection of molecular models suggested

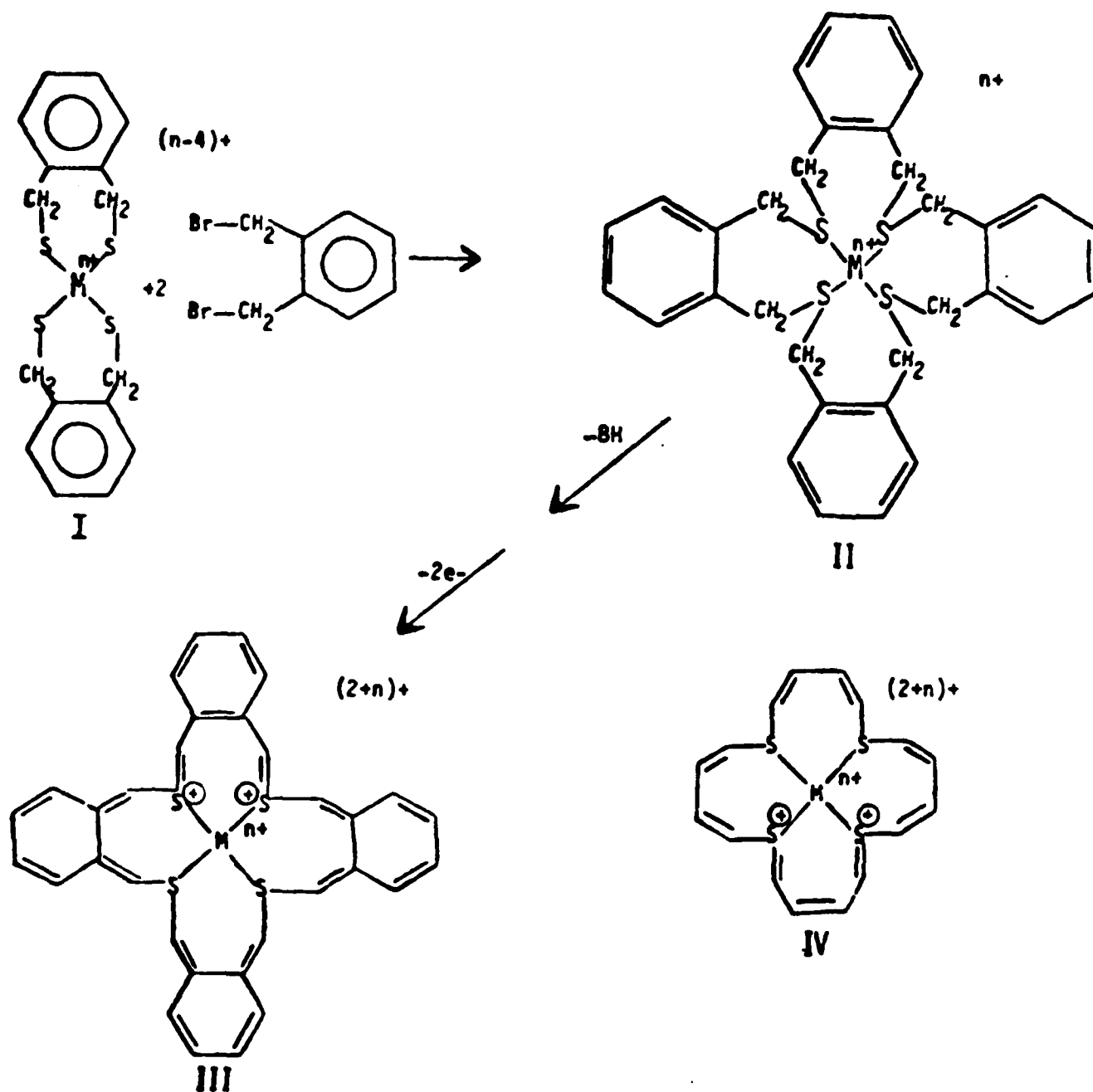


Figure 2. Proposed synthesis route to new sulfur macrocycles.

that this, presumably tetrahedral, cobalt complex could also provide the necessary geometrical requirements for the template reaction with the α,α' -dibromo-o-xylene as illustrated in Figure 2. Several attempts to carry out this reaction, however, using the preformed and characterized cobalt(II) complex, yielded only the starting materials and uncharacterized decomposition products. These efforts to obtain sulfur macrocycles were subsequently abandoned in favor of another approach to the synthesis of new transition metal complex containing solid state systems described below.

B. Synthesis of a New Chelating Ligand

In work not related to the current contract effort also going on in our laboratory a new organic ligand system has been recently synthesized. This ligand, illustrated in Fig. 3a, is a derivative of 1,10-phenanthroline which has been substituted with dicyanomethylene groups in the 4,7-positions. It was obtained from the corresponding 4,7-dichloro-1,10-phenanthroline by reaction with $\text{Na}^+ \text{HC}(\text{CN})_2^-$ and has been characterized as the dianion $\text{C}_{18}\text{H}_6\text{N}_6^{2-}$ in various complexes with Na^+ , Li^+ , and Ru^{2+} .⁽⁷⁾ It can potentially exist in several different oxidation states, with the dianion as the most reduced form. When coordinated to Ru in the complex, $(\text{o-phen})_2\text{Ru}(\text{C}_{18}\text{H}_6\text{N}_6)$, this ligand in fact undergoes two sequential, electrochemically reversible, one-electron oxidations.

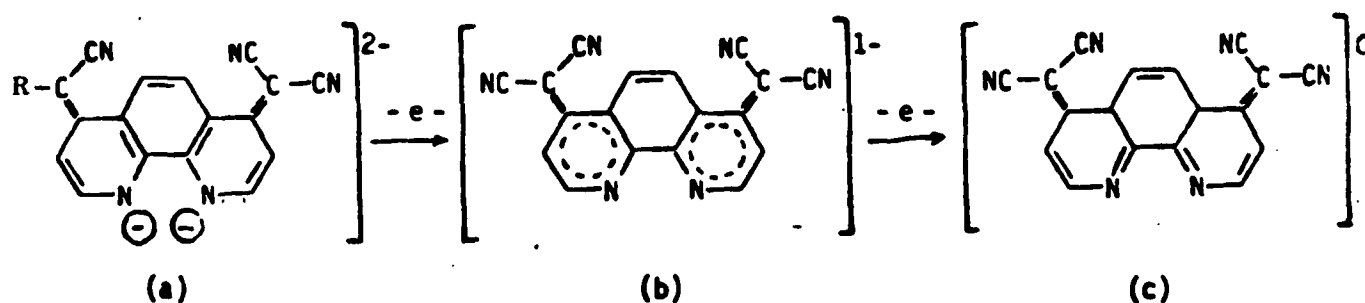


Figure 3. Possible redox series deriving from oxidation of the 4,7-bis(dicyanomethylidene)-4,7-dihydro-1,10-phenanthroline ligand ($\text{C}_{18}\text{H}_6\text{N}_6^{2-}$).

It is of interest here as a possible constituent of square planar metal complexes which could assume a 1-D stacking arrangement in the solid state and undergo partial oxidation to yield highly conductive 1-D materials. Two possible complexes of this type are the platinum(II) and iridium(I) species illustrated in Figure 4:

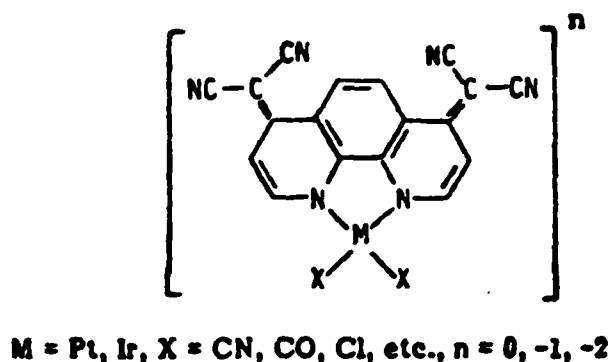


Figure 4

Initial work focused on the preparation of the platinum(II) complexes, starting from both PtCl_4^{2-} and $\text{Pt}(\text{CO})_2\text{Cl}_2$. The latter compound on reaction with the $\text{C}_{18}\text{H}_6\text{N}_6^{2-}$ ligand (L) has yielded a new Pt(II) complex for which elemental analysis suggests a $(\text{Et}_4\text{N})_2\text{LPtCl}_2$ composition; however, efforts to purify this complex by recrystallization and characterize it more fully have not yet been successful.

Subsequently a modification of a preparation reported in the literature for $\text{Ir}(\text{CO})_2\text{Cl}_2^-$ has been employed to obtain a new Ir(I) complex of this $\text{C}_{18}\text{H}_6\text{N}_6^{2-}$ ligand, of the type $\text{R}^+\text{Ir}(\text{C}_{18}\text{H}_6\text{N}_6)(\text{CO})_2^-$, where R^+ = various inorganic and organic monocations. The IR spectra of this complex is consistent with the presence of a cis-planar arrangement of two CO groups and show clearly the characteristic CN stretching frequencies of the coordinated $\text{C}_{18}\text{H}_6\text{N}_6^{2-}$ ligand. The ^1H nmr spectrum of the Et_4N^+ salt shows the expected five peaks (a singlet

and a pair of doublets) due to the $C_{18}H_6N_6^{2-}$ ligand as well as those attributable to the Et_4N^+ ion. Elemental analysis of this compound is also consistent with the $Et_4N^+Ir(C_{18}H_6N_6)(CO)_2^-$ formulation.

This compound was converted to various other $R^+Ir(C_{18}H_6N_6)(CO)_2^-$ salts by metathesis in CH_3NO_2 solution. None of these salts have been obtained thus far in the form of single crystals suitable for x-ray diffraction or conductivity studies; however, they have been characterized by x-ray powder diffraction and elemental analyses and preliminary conductivity studies have been performed using compacted polycrystalline samples. These studies indicate conductivities in the range of insulators to semiconductors for the various compounds with individual variations that may reflect differences in the structures and, in particular, the $Ir(C_{18}H_6N_6)(CO)_2^-$ stacking in the solid state.

The redox behavior of this system was also investigated by cyclic voltametry on the $Et_4N^+Ir(C_{18}H_6N_6)(CO)_2^-$ salt in CH_3CN solution. Reversible redox reactions were not observed; however three non-reversible oxidations were noted at $\sim +0.5$, $+1.0$ and $+1.6$ v vs. SCE.

Upon treatment with iodine in CH_3CN/CH_2Cl_2 solution changes in the x-ray powder diffraction patterns and physical appearance of each of these salts were observed. Preliminary measurements of their electrical conductivities in the form of polycrystalline compacts indicates a substantial increase relative to the unoxidized salts, in general, with the highest value observed in the case of the $Li^+[Ir(C_{18}H_6N_6)(CO)_2^-]_x$ derivative at $1.8 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$. Considering that the conductivity of polycrystalline samples are usually a factor of $10^2 \rightarrow 10^3$ less than that in the single crystals, this value is approaching the range found for many so-called "1-D metal" systems and suggests the existence of substantial inter-molecular orbital overlap in this system as well as the presence of a significant

number of charge carriers. The conductivity data on this and the various other $R^+ [Ir(C_{18}H_6N_6)(CO)_2]^-$ salts before and after oxidation with iodine are summarized in Table I.

Further work on this system must await the availability of single crystals suitable for more detailed structural and conductivity studies. Efforts to obtain such crystals are continuing as well as attempts to prepare other examples of planar $C_{18}H_6N_6^{2-}$ complexes.

TABLE I**Conductivity Data for $\text{Ir}(\text{CO})_2(\text{C}_{18}\text{H}_6\text{N}_6)^-$ Complexes**

Compound	Conductivity($\text{ohm}^{-1}\text{cm}^{-1}$)*
$\text{Et}_4\text{N}^+[\text{Ir}(\text{CO})_2(\text{C}_{18}\text{H}_6\text{N}_6)^-]$	1.4×10^{-8}
$\text{MeQuin}^+[\text{Ir}(\text{CO})_2(\text{C}_{18}\text{H}_6\text{N}_6)^-]$	6.0×10^{-8}
$\text{MeQuin}^+[\text{Ir}(\text{CO})_2(\text{C}_{18}\text{H}_6\text{N}_6)^-]\text{I}_x$	6.3×10^{-5}
$\text{Acr}^+[\text{Ir}(\text{CO})_2(\text{C}_{18}\text{H}_6\text{N}_6)^-]$	3.6×10^{-8}
$\text{Acr}^+[\text{Ir}(\text{CO})_2(\text{C}_{18}\text{H}_6\text{N}_6)^-]\text{I}_x$	6.8×10^{-5}
$\text{Li}^+[\text{Ir}(\text{CO})_2(\text{C}_{18}\text{H}_6\text{N}_6)^-]$	4.6×10^{-7}
$\text{Li}^+[\text{Ir}(\text{CO})_2(\text{C}_{18}\text{H}_6\text{N}_6)^-]\text{I}_x$	1.8×10^{-3}

*Pressed Powder Measurements at Room Temperature

Section 3

OTHER ACTIVITIES

During the period of this contract Dr. Interrante has served as Secretary-Treasurer, Chairman-elect and Chairman of the Division of Inorganic Chemistry, ACS. He has also served on the Inorganic Subcommittee of the ACS Examinations Committee which was responsible for the preparation of an examination for nationwide use in the advising and placement of beginning graduate students in chemistry.

He is currently a member of the Inorganic Syntheses Corporation and participates in the evaluation of prospective manuscripts for inclusion in this series. He was recently asked to serve on the NSF sponsored National Main-Group Chemistry Workshop and has been involved in the process of selecting topics and participants for the 1982 and 1983 workshop meetings. Dr. Interrante has presented many invited lectures on his contract-related research at various meetings and universities. During the past 3 years these talks have included a Section Lecture at the XXI International Conference on Coordination Chemistry, the 1980 Vernon Lecture at Northeastern University and the 1981 Almquist Lecture of the University of Idaho.

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(Published under previous contract F44620-76-C-0006,
"Solid State Materials Derived from Planar Metal Complexes")

1. "Magnetic Field Effects on TTF $\text{CuS}_4\text{C}_4(\text{CF}_3)_4$. A Spin-Peierls System", J.W. Bray, I.S. Jacobs, D. Bloch, D.E. Moncton, D.E. Shirane, J.C. Bonner and L.V. Interrante, *Phys. Rev. B* **20**, 2067 (1979).

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1. "Spin-Peierls Phase Diagrams: Observations and Models", I.S. Jacobs, L.V. Interrante, D. Bloch, J.C. Bonner, J.W. Bray and H.R. Hart, Jr., *J. Magnetism and Magnetic Matls.* **158**, 332 (1980).
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8. "New π -Donor-Acceptor Compounds Derived from a Macrocyclic Planar Metal Complex", P. Cassoux, L.V. Interrante and J.S. Kasper, *Proc. Intn'l. Conference on Low-Dimensional Conductors, Molecular Crystals & Liquid Crystals*, in press (1982).

TALKS GIVEN

1. "Molecular Solids with Unusual Solid State Properties. π -Donor-Acceptor Compounds of Organic Molecules with Planar Metal Complexes." Invited talk at Solar Energy Research Institute, Golden, CO on July 2, 1979.
2. "Charge Transfer Salts Derived from Organic π -Donors and Metal Complex π -Acceptors". Invited paper at the Wurster's Centennial Symposium, Washington, D.C., ACS Meeting, September 12, 1979.
- 3,4. "Molecular Solids with Unusual Solid State Properties. π -Donor-Acceptor Compounds of Organic Molecules with Planar Metal Complexes". Inorganic Chemistry Seminar, Pennsylvania State University, April 21, 1980; and 1980 Vernon Lecture Presentation at Northeastern University, Department of Chemistry, May 1, 1980.
- 5,6. "Coordination Compounds as a Source of Electrically Conductive Solid State Materials". Invited Section Lecture, XXI International Conference on Coordination Chemistry, Toulouse, France, July 9, 1980; and Seminar at State University of New York at Albany, November 4, 1980.
- 7-10. "Coordination Compounds as a Source of Electrically Conductive Solid State Materials". Argonne National Lab., April 13, 1981; North Dakota State University, April 15, 1981; Univ. of Minnesota, April 16, 1981; Univ. of Massachusetts, Amherst, May 18, 1981; Group de Recherche sur les Semiconducteurs et les Dielectriques, College Militaire Royal, St. Jean, Quebec, Canada, June 10, 1981.
11. "Synthesis and Solid State Properties of a New Planar Iridium(I) Complex". International Conference on Low-Dimensional Conductors, Boulder, CO, August 13, 1981.
12. "Long-Range Research in Industry: A Personal Perspective". 1981 Almquist Lecture, University of Idaho, Moscow, October 22, 1981.
13. "On a Novel Organic Ligand System and Its Complexes with Ru(II) and Ir(I)", University of California at Berkeley, October 23, 1981.
14. "Lower Dimensions in Solid State Chemistry: Synthesis and Study of Quasi-One and Two-Dimensional Materials", University of California at Santa Barbara, November 2, 1981.

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